First Principles Calculations of Existing and Novel Materials

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2020 DOE VTO Annual Merit Review

June 1-4, 2020

Project ID: bat054

LAWRENCE BERKELEY NATIONAL LABORATORY

Overview

Timeline

- Start date: October 2016
- End date: September 2020
- Percent complete: 75%

Budget

- Total project funding
  -- FY20 $350,000

Barriers Addressed

- Energy density
- Cycle life
- Cost

Partners

- none

Relevance/Objectives

Impact:

- To make solid-state batteries we need conductors that combine good electrochemical properties with processability.

- By understanding the factors that control Li-ion motion in crystalline and amorphous solids, and electrochemical stability, we will be able to understand better how processing influences performance

Objectives:

- Understand the role of local structure on ionic conductivity and use to find the optimal amorphous LPS.

- Understand the interface reactivity of LPS with electrodes, and design suitable coating materials to avoid harmful interface reaction.

- Develop rational design principle to engineer the structure and composition of LPS electrolyte.

Milestones

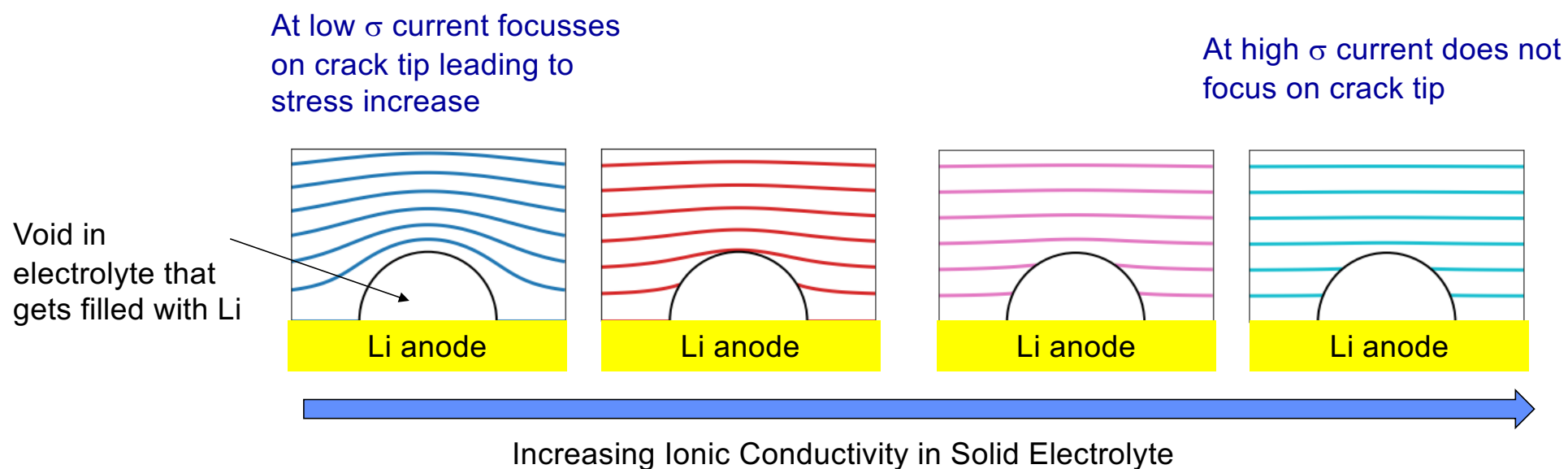| Date	Milestones	Status
December 2019	Modeling of the Li_2S-P_2S_5 ground state phase diagram for SSEs: solid phases correctly modeled	Completed
March 2020	Modeling of LPS Li mobility in amorphous state with variations of PS_4 structural units	Completed
June 2020	Develop model for the Li conductivity in amorphous sulfide solids	On schedule
September 2020	Modeling of the full finite temperature L-S-P phase diagram to understand metastability of the highly conducting solids	On schedule

Approach

- Construct the Li-P-S phase diagram to understand stability of crystalline phase.

- Model amorphous LPS and identify the common local structure motifs and relate to ionic conductivity

- Identify suitable coating material to minimize the reaction between LPS and cathode during cycling

Methods

- DFT with GGA and SCAN functional for energy calculations. Molecular Dynamics for Li-transport

- Phonon calculations with harmonic approximation for vibrational contribution to free energy.

- Simulation of PDF and Raman/IR spectroscopy to capture the structural features of different LPS phases.

- High throughput computational study of reaction energy of coating materials with LPS.

Importance of High Ionic Conductivity in Solid Electrolytes

- Lowering of impedance in cell

- High ionic conductivity also makes SE more fault tolerant by screening away any stress concentrations arising from defects

At low σ current focusses on crack tip leading to stress increase

At high σ current does not focus on crack tip

Void in electrolyte that gets filled with Li

Li anode   Li anode   Li anode   Li anode

Increasing Ionic Conductivity in Solid Electrolyte

Amorphous Electrolytes

Advantages

- No grain boundaries and potentially less boundary resistance
- Less Li penetration ? LiPON is only amorphous electrolyte currently, and it shows resistance to Li penetration
- Significant variability possible in composition and structure

Disadvantages

- Difficult to structurally characterize
- More difficult to understand what controls conductivity
- More difficult for process control
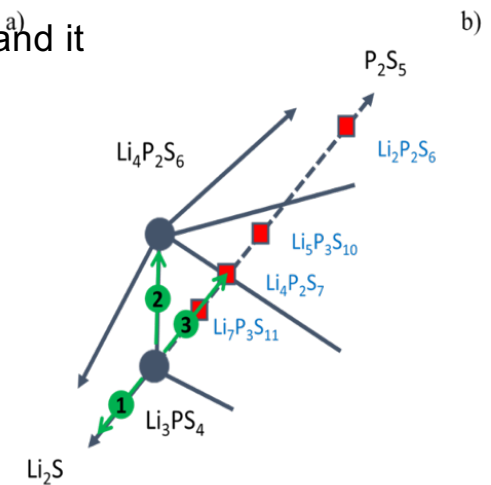
Focus on LPS (Li-thiophosphates) as they are soft, low density, and inexpensive

What controls conductivity in Crystalline and amorphous Li-P-S phases (Exp data)

x(Li$_2$S) + (100-x)(P$_2$S$_5$)	Phase	Space group	Ionic conductivity (S cm^{-1}) at 25°C	Building blocks	References
67*	Li$_4$P$_2$S$_6$ (+S)	P-31m	2.9 × 10^{-11}	P$_2$S$_6$$^{4-}$	[1]
70	Li$_7$P$_3$S$_{11}$	P-1	1.7 × 10^{-2}	P$_2$S$_7$$^{4-}$, PS$_4$$^{3-}$	[2, 3]
75	β-Li$_3$PS$_4$	Pnma	1.6 × 10^{-4}	PS$_4$$^{3-}$	[4]
70	Glass	-	4 × 10^{-5}	(P$_2$S$_6$)$^{4-}$, (PS$_4$)$^{3-}$, (P$_2$S$_7$)$^{4-}$	[5, 6]
75	Glass	-	6 × 10^{-4}	(P$_2$S$_6$)$^{4-}$, (PS$_4$)$^{3-}$, (P$_2$S$_7$)$^{4-}$	[5, 6]
80	Glass	-	2 × 10^{-4}	(P$_2$S$_6$)$^{4-}$, (PS$_4$)$^{3-}$, (P$_2$S$_7$)$^{4-}$	[5, 6]

[1] C. Dietrich *et al., Chem. Mater., 28*, 8764 (2016); [2] Y. Seino *et al., Energy Environ. Sci., 7*, 627 (2014); [3] I.H. Chu *et al., ACS Appl. Mater. Interfaces*, 8, 7843 (2016); [4] Z. Liu *et al., J. Am. Chem. Soc.*, 135, 975 (2013); [5] A. Hayashi et al., J. Am. Ceram. Soc., 84, 477 (2001); [6] O.U. Kudu et al., J. Power Sources, 407, 31 (2018)

- Crystalline phases having specific building blocks (PS$_4$$^{3-}$, P$_2S_7$$^{4-}$) show high (10^{-3} ~ 10^{-4} S$\cdot$cm^{-1}) conductivity

- Same building blocks were found in highly conducting amorphous materials (Li$_2$S composition 70~80 at.%)

- The building blocks are suggested to have a role on ionic conductivity

C. Dietrich *et al., J. Mater. Chem. A,* 5, 18111 (2017)
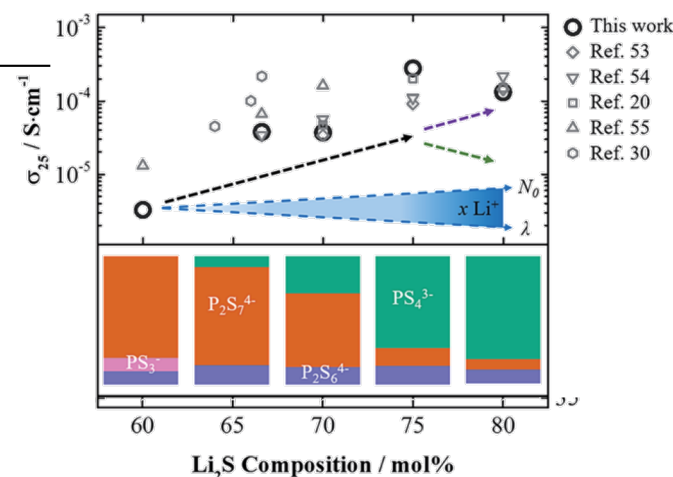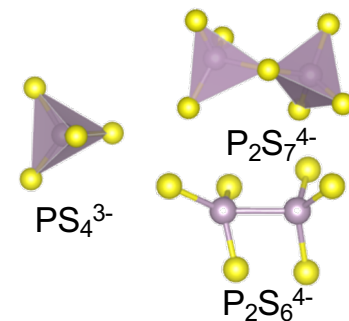
Different local structures (from ^{31}P MAS NMR) in glassy xLi$_2$S-(1-x)P$_2$S$_5$ from ball-milling:

Modeling: Create amorphous LPS structures with different building blocks

Condensation of PS_4^{3-} units with free S^{2-} formation →

Condensation of PS_4^{3-} units with S^{2-} removal →

	Amorphous, 1.8 and 2.0 g cm^{-3} (nickname)		Crystalline
Stoichiometry $Li_2S : P_2S_5$ = 75 : 25	$48Li^+ + 16PS_4^{3-}$ from β-Li_3PS_4 $48Li^+ + 14PS_4^{3-} + P_2S_7^{4-} + S^{2-}$ $48Li^+ + 14PS_4^{3-} + P_2S_6^{4-} + (2S)^{2-}$ $48Li^+ + 12PS_4^{3-} + 2P_2S_7^{4-} + 2S^{2-}$ $48Li^+ + 16PS_4^{3-}$ random orientation	β-PS_4 $1P_2S_7$ $1P_2S_6$ $2P_2S_7$ r-PS_4	α-Li_3PS_4 β-Li_3PS_4 γ-Li_3PS_4
Off-stoichiometry	$48Li^+ + 14PS_4^{3-} + P_2S_7^{4-} - 2e^-$ $48Li^+ + 14PS_4^{3-} + P_2S_6^{4-} - 2e^-$ $48Li^+ + 12PS_4^{3-} + 2P_2S_7^{4-} - 4e^-$ $48Li^+ + 12PS_4^{3-} + 2P_2S_6^{4-} - 4e^-$	$1P_2S_7$ -S $1P_2S_6$ -2S $2P_2S_7$ -2S $2P_2S_6$ -4S	$Li_7P_3S_{11}$

- Structures with different anion building block were generated and simulated using AIMD

- Stoichiometries are fixed to **$Li_3PS_{4-\delta}$** to maintain the same concentration of Li. Charge neutrality imposed with background charge.

- **All amorphous structures are annealed to 1000 K**, which does not destroy P-S polyanion, and quenched to simulation temperatures

- AIMD simulations are performed for more than 250 ps at 600-1000 K

# Structure verification with experiment - pair distribution function
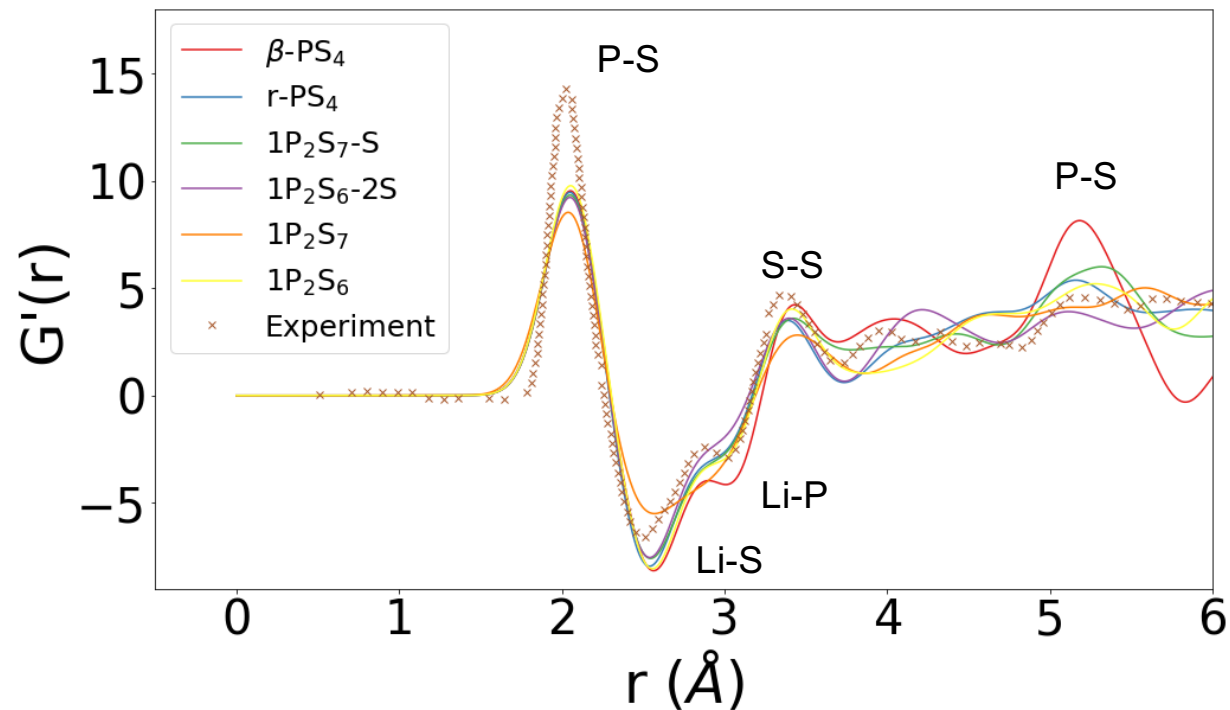
- Main peak positions of simulated structures match well with those of the experiment

- Small peaks of each structure are found in the experimental result, probably because it contains characteristics of the different simulated structures

Exp.: K. Ohara *et al., Sci. Rep.,* 6, 21302 (2016)

Calculated Ionic conductivities at 300 K
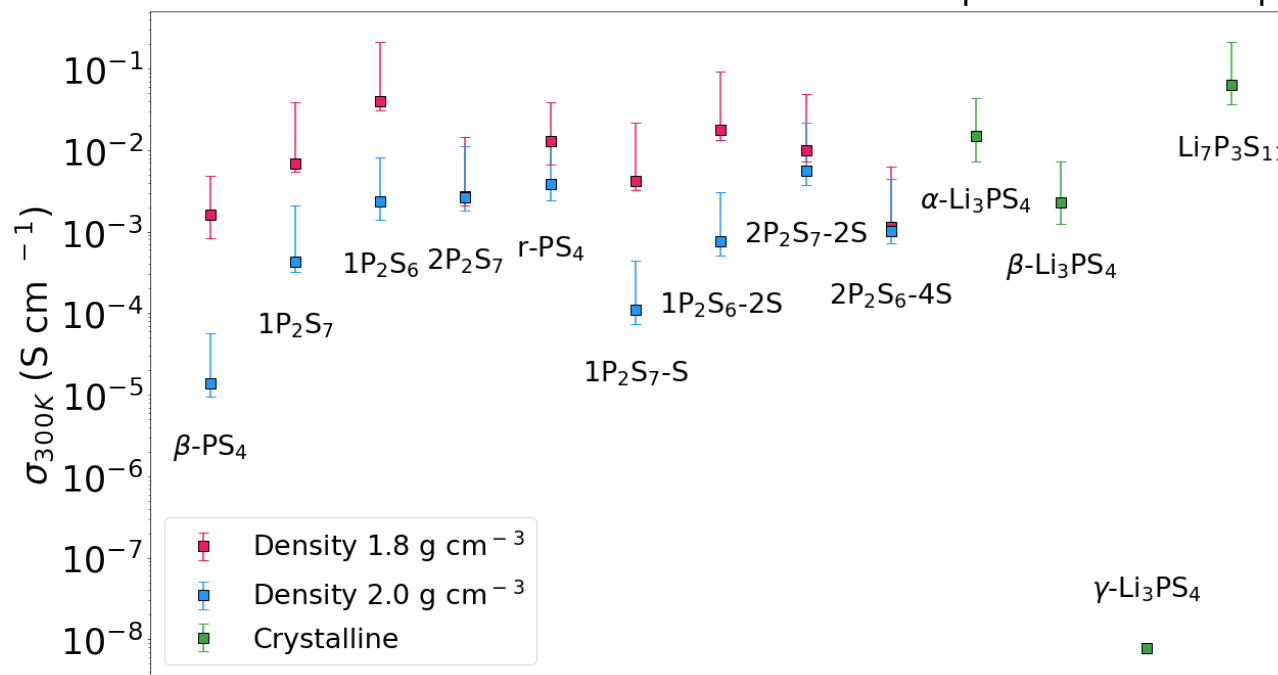
- Calculated ionic conductivities agree well with experimental value.

- Two densities were probed (1.8 and 2g/cm^{-3}). Lower density gives higher conductivity, but largely same trend with chemistry

- There is **no obvious trend** between **the polyanion ratio and ionic conductivity**

- **Therefore, the effect of chemistry on Li-conductivity is more complex and the effect of the more long-ranged structure needs to be considered (how the P-S units are connected)**

Tracking effectiveness of Li ions motion

For each structure we count the number of Li ions that are immobile or very slow in the simulation.
The best conductor have almost no slow Li ions meaning that they are fully frustrated in their energy landscape (no Li gets trapped)

Anion composition	# of immobile Li (per 48 Li, 100 ps)	# of slow Li (per 48 Li, 100 ps)	Conductivity at 300K ($S \cdot cm^{-1}$)
β-PS_4	0	6	$1.55 * 10^{-3}$
$1P_2S_7$	0	3	$6.95 * 10^{-3}$
$1P_2S_6$	0	1	$4.04 * 10^{-2}$
$2P_2S_7$	0	8	$2.68 * 10^{-3}$
r-PS_4	0	1	$1.29 * 10^{-2}$
$1P_2S_7 - S$	0	2	$4.24 * 10^{-3}$
$1P_2S_6 - 2S$	0	2	$1.77 * 10^{-2}$
$2P_2S_7 - 2S$	0	1	$9.91 * 10^{-3}$
$2P_2S_6 - 4S$	1	8	$1.14 * 10^{-3}$

- In amorphous structure, almost **all Li atoms are "mobile"**, undergoing jumps, implying **frustrated Li energy landscape**
- The number of Li atoms, which **actually travel** far away from its original position, largely **differs with the structure**, determining the ionic conductivity
- The influence of polyanion ratio on Li diffusion path should be analyzed -- ongoing
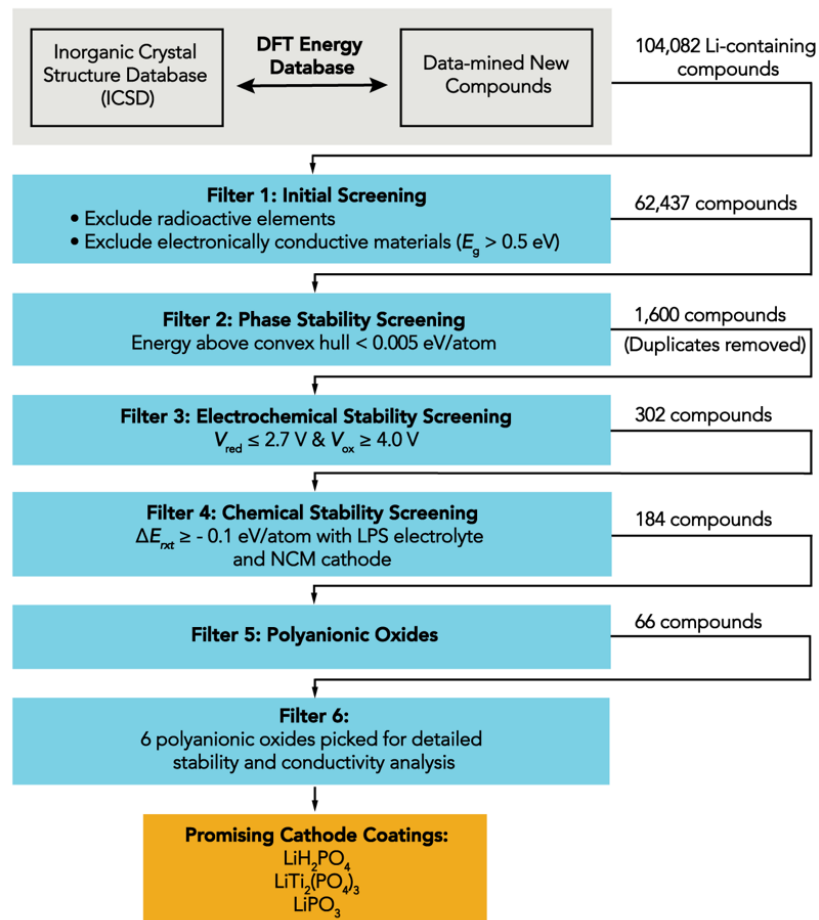
Problem for sulfides is anodic stability (< 2.5V). Cathode coatings needed

Computational Screening of > 100,000 compounds
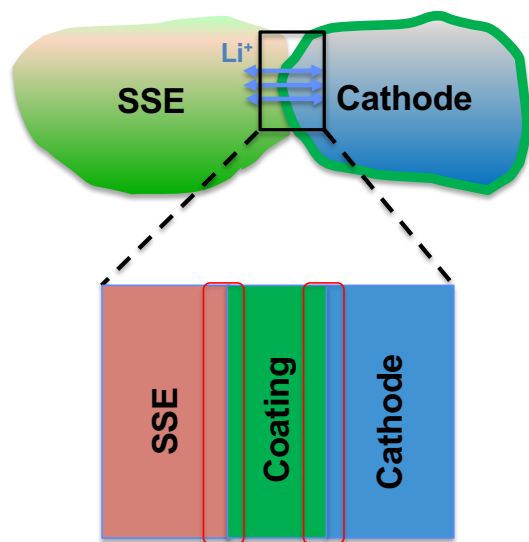
Search for good coating materials between NMC cathode and LPS electrolyte

- Reduction stability limit ≤ 2.7 V
- Chemical stability with SSE

- Oxidation stability limit ≥ 4.0 V
- Chemical stability with cathode

| Inorganic Crystal Structure Database (ICSD) | DFT Energy Database | Data-mined New Compounds | 104,082 Li-containing compounds |

Filter 1: Initial Screening
- Exclude radioactive elements
- Exclude electronically conductive materials ($E_g > 0.5$ eV)

62,437 compounds

Filter 2: Phase Stability Screening
Energy above convex hull < 0.005 eV/atom

1,600 compounds
(Duplicates removed)

Filter 3: Electrochemical Stability Screening
$V_{red} \leq 2.7$ V & $V_{ox} \geq 4.0$ V

302 compounds

Filter 4: Chemical Stability Screening
$\Delta E_{rxt} \geq -0.1$ eV/atom with LPS electrolyte and NCM cathode

184 compounds

Filter 5: Polyanionic Oxides

66 compounds

Filter 6:
6 polyanionic oxides picked for detailed stability and conductivity analysis

Promising Cathode Coatings:
LiH_2PO_4
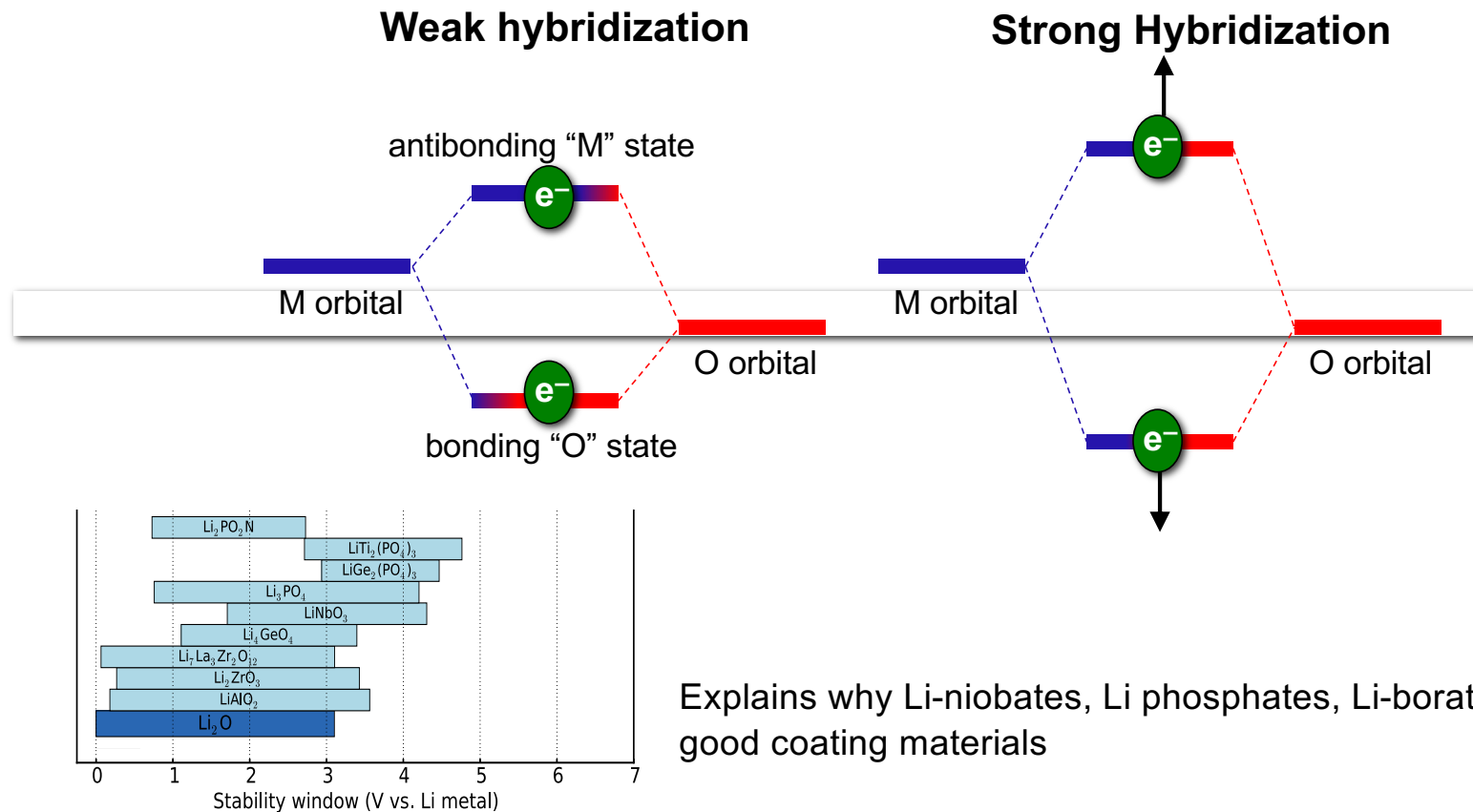$LiTi_2(PO_4)_3$
$LiPO_3$

Polyanionic oxides have better oxidation stability than oxides

**Stability window of stable Li-containing materials**
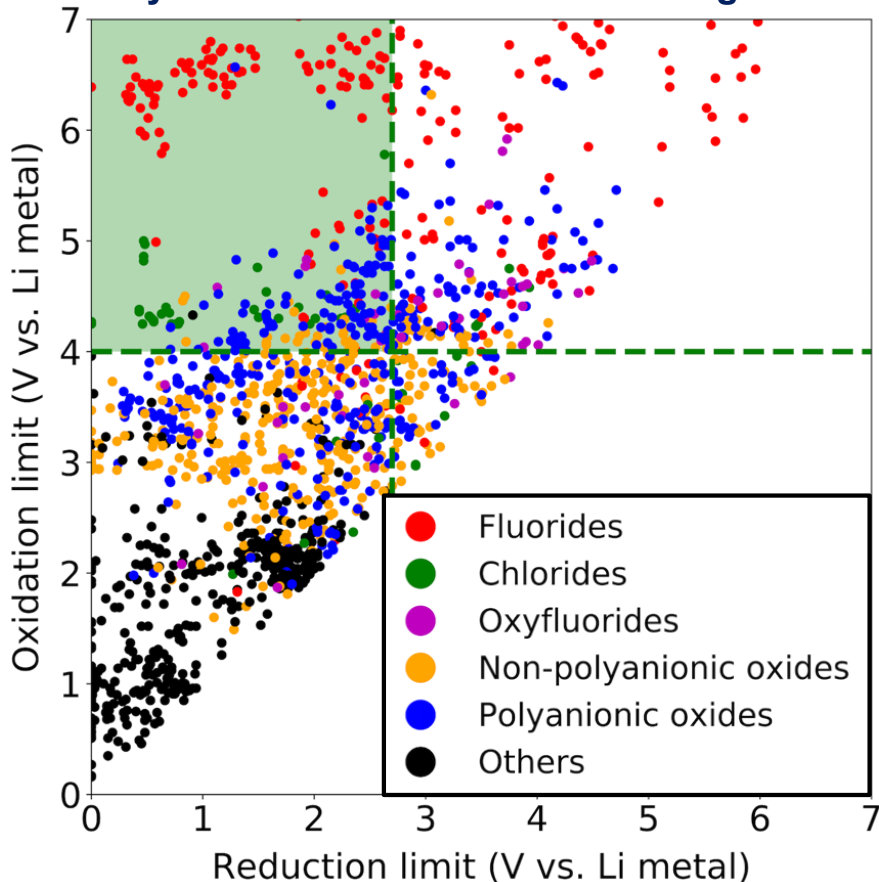
- Vertical separation of different chemistries.

- **Fluorides** have > 6 V oxidation stability.

- Nitrides, sulfides have < 3 V oxidation stability, not stable at high cathode voltage.

- **Polyanionic oxides** have higher oxidation limits than **non-polyanionic oxides**.

# The stronger the hybridization of a metal with the anion the higher the oxidation limit

Weak hybridization

Strong Hybridization

antibonding "M" state

M orbital

O orbital

bonding "O" state

M orbital

O orbital

Explains why Li-niobates, Li phosphates, Li-borates etc are good coating materials

Li_2PO_2N

$LiTi_2(PO_4)_3$

$LiGe_2(PO_4)_3$

Li_3PO_4

$LiNbO_3$

Li_4GeO_4

$Li_7La_3Zr_2O_{12}$

Li_2ZrO_3

$LiAlO_2$

Li_2O

0   1   2   3   4   5   6   7

Stability window (V vs. Li metal)

Experimental confirmation: Comparison of Li-Zr-O coated NMC with Li-borate coated NMC

Cycle life testing in LPS/coated-NMC solid state cell (0.05 mA cm^{-2} between 2.5 and 4.3v) V
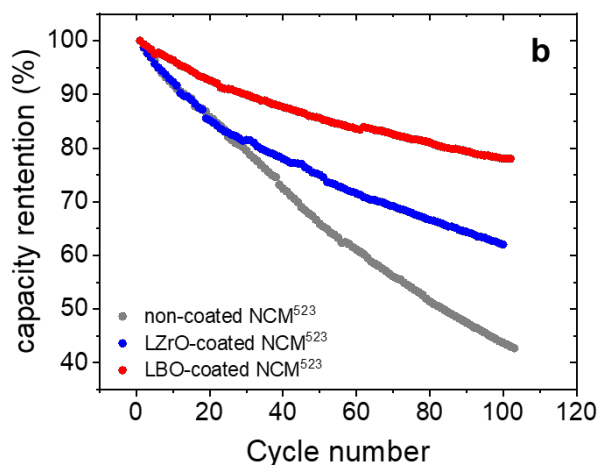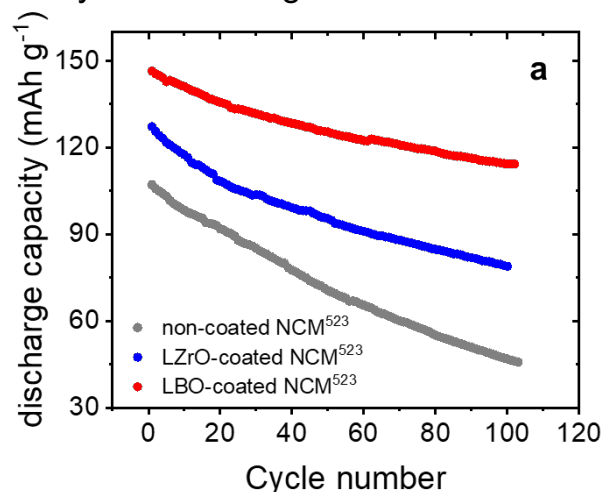
Much better cycling is achieved with LBO-coated NMC
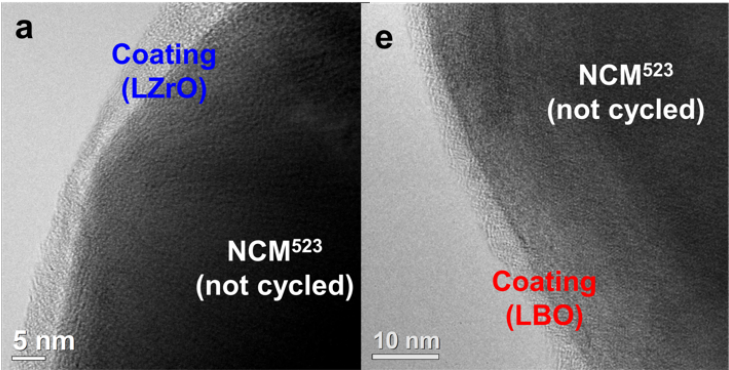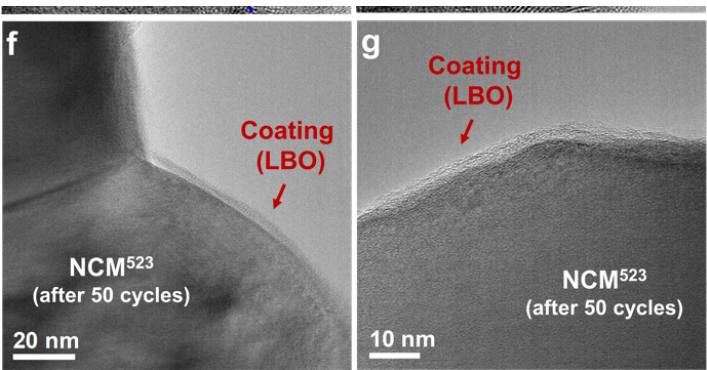
Computed stability limits
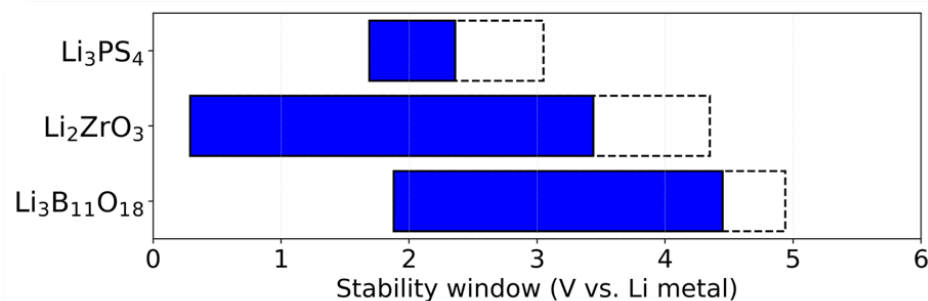
Ab initio computations predict that LZO coating will break down above 3.5V whereas LBO coating is stable above 4V

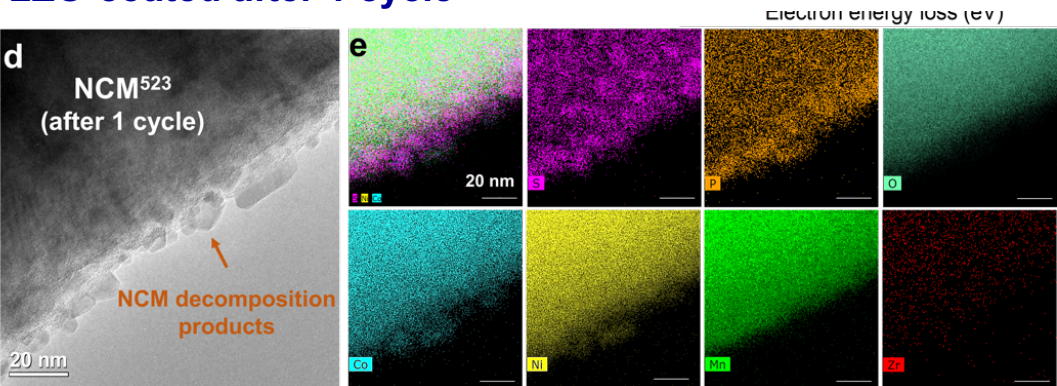# Experimental confirmation of LZO coating break-down in first charge

Pristine coating on uncycled materials

LBO-coated after 50 cycles
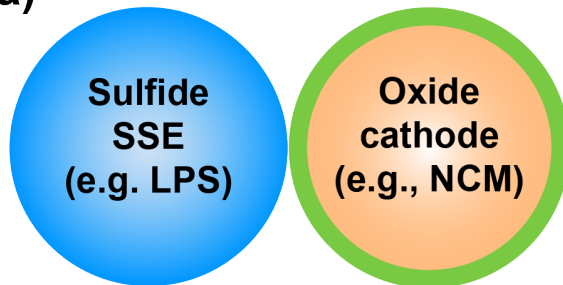

LZO-coated after 1 cycle

LBO coating remains intact even after 50 cycles

LZO coating breaks down after first cycle and leads to reactivity of NMC with LPS

Work with Mary Scott at NCEM/LBNL
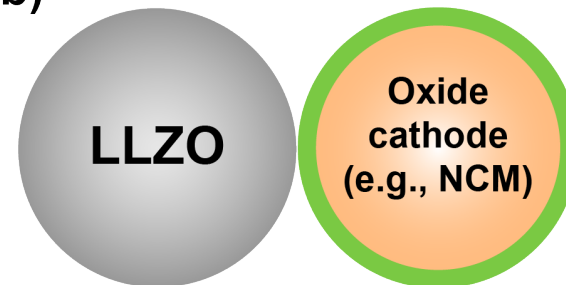
Coating recommendations

(a)

Sulfide SSE (e.g. LPS)

Oxide cathode (e.g., NCM)

Sintering/Hot-pressing/Cold-pressing
• Borates
• Phosphates

(b)

LLZO

Oxide cathode (e.g., NCM)

Sintering/Hot-pressing
• Borates
• Oxides (when charging voltage is limited)

(c)

Sulfide SSE (e.g. LPS)

LFPO
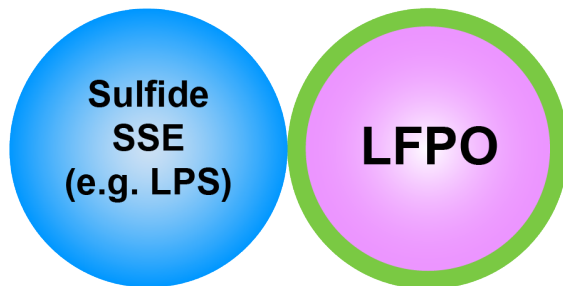
Sintering/Hot-pressing/Cold-pressing
• Borates
• Phosphates

(d)

LLZO

LFPO
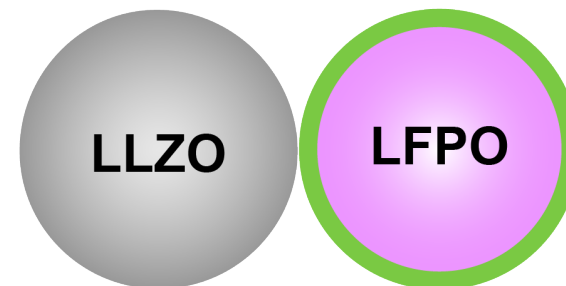
Sintering/Hot-pressing
• Borates
• Oxides

Responses to Previous Year Reviewers' Comments

We thank the reviewers from last year for providing comments. The majority of the comments was highly positive. One reviewer commented that collaboration with experimentalists should be expanded. In response we have performed a TEM study with Mary Scott at NCEM to investigate the stability and degradation mechanism of coating materials on NMC in contact with LPS solid electrolyte

Contributors and Collaborators

Gao Liu : investigation of solution processed LPS

Mary Scott and Yaqian Zhang (NCEM): Investigation of coating stability and breakdown when cycling in a solid state battery

Remaining Challenges and Barriers

- Amorphous structures are challenging to structurally characterize and understand.

Proposed Future Work

- We will model extended amorphous structures to investigate how the connectivity of the various P-S groups influences conductivity

- Start percolation analysis on these large structures

- Also move towards larger-scale search for novel crystalline conductors with high conductivity

"Any proposed future work is subject to changes based on funding levels."

Summary

- Ab initio molecular dynamics simulations show that the effect of structure on the Li conductivity in amorphous LPS is more complex than simply amount of various P-S groups presents.

- Transport seems to be influenced by the longer range connectivity of these groups. This may be related to the fact that some very good conductors in this family are glass-ceramics.

- Low anodic stability of sulfides can be addressed by suitable coating materials on NMC cathodes

- Coating requirements for solid state batteries are different from those in liquid cells due to the higher chemical reactivity with the solid electrolyte as compared to the liquid electrolytes. For sulfide electrolytes the chemical reactivity is largely driven by exchange of O (from the cathode) with S (from the SE) to form PO_4 groups.

- Regular oxide coating materials (such as Li-Zr-O) are not stable at typical NMC charging voltage (4.3V). Polyanion coatings, such as Li-borate show excellent long-cycle stability at 4.3V.